

**DEVELOPMENT OF NONCHROMATE CORROSION INHIBITORS FOR
COATINGS ON ALUMINUM**

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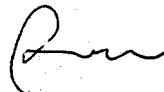
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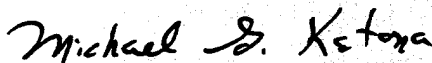
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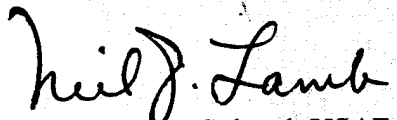
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The objective of this study was to develop nonchromate substitutes equivalent to the chromate corrosion inhibitors formulated in primers and/or paints for the protection of high-strength aluminum alloys. Quaternary ammonium dimolybdate salts (Q-Mo) were found to prevent ocean-water salt-spray corrosion for 2000 hours, equivalent to the strontium chromate-filled epoxy-polyamide primer, MIL-P-23377. Quaternary ammonium nitrate, phosphate, and borates were included in the evaluations. However, the Q-Mo was superior in every regard. The dimolybdate quaternary ammonium salt is a developmental inhibitor of high purity containing less than 1000 ppm sulfate and 100 ppm chloride. Optimization of the molybdate in the primer was eminently successful in achieving the physical, corrosion, and fluid resistance, and working properties required for demonstration testing and evaluation.					
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PREFACE

This report was prepared by the Research & Development Division, Lockheed Missiles & Space Company, Inc. (LMSC), Palo Alto, California, for the Air Force Civil Engineering Support Agency, Engineering and Services Laboratory, Tyndall Air Force Base, Florida 32403-6001.

The report summarizes work performed between February 1990 and March 1993 under contract F08635-90-C-0283. Lieutenant Phillip P. Brown was the AL/EQS-OL project officer. Dr. L. J. Bailin was principal investigator, LMSC.

The report was submitted by the author 31 March 1993. Special assistance to the project was provided by Mr. Dan Bernard, Deft Coatings, Irvine, California, and Dr. Fred Gadberry, Akzo Chemical, Dobbs Ferry, New York.

EXECUTIVE SUMMARY

A. OBJECTIVE

The primary objective of the program was twofold: first, to replace inorganic strontium chromate as a corrosion inhibitor in primers and coatings of interest to the Air Force; second, to prove the efficacy of the replacement inhibitors selected for the epoxy-polyamide primer.

B. OBJECTIVE

For many years, the EPA has recognized the health hazards of chromates and chromium(IV) compounds related to carcinogenicity, mutagenicity, and general toxicity. Many investigations have been conducted to find suitable substitutes for these chromium compounds. Water-soluble hydrophilic anionic substitutes have been used in coolants and cooling towers. For applications to conventional oil-base paint medium, the corrosion inhibitor must then be organophilic.

Quaternary ammonium chromate salts have been used previously as corrosion inhibitors for oil and gas production. The quaternary ammonium salts with nonchromate anions can be similarly prepared and used as nonchromate corrosion inhibitors.

C. SCOPE

Four quaternary ammonium salts, i.e., nitrate, hydrogen phosphate, borate, and molybdate, and their variations, were selected and tested for their suitability as nonchromate corrosion inhibitors for aluminum alloys. Testing included (1) initial electrochemical evaluation of the anions in aqueous media; (2) direct deposition of the quaternary ammonium salts on aluminum alloy surfaces, followed by top-coating with epoxy-polyamide and exposure to an ASTM B-117 salt spray; and (3) formulating the quaternary ammonium salts in a MIL-P-23377 primer, followed by testing according to specification and in an ASTM B-117 system using Pacific Ocean water in place of sodium chloride solution.

D. METHODOLOGY

The commercial nonchromate corrosion inhibitors evaluated under this program were:

- (1) Quaternary ammonium nitrate (Sherex EP SC-150-165, Henkel Aliquat 336N)
- (2) Quaternary ammonium hydrogen phosphate (Sherex EP SC-303-1130)
- (3) Quaternary ammonium borate (Sherex EP SC-303-60, Akzo RD 5444A)
- (4) Quaternary ammonium dimolybdate (Sherex EP SC-150-121, Akzo Acar 92017)

Electrochemical corrosion and coating evaluations were the principal methods used to assess the performance of these inhibitors. The electrochemical processes involved the anions only, but the panel coating evaluations included the complete formulated salts.

E. TEST DESCRIPTION

Corrosion screening tests were performed in accordance with ASTM G3-89 on solutions containing 3.5-percent sodium chloride with 500 ppm of the specified inhibitor added as the sodium salt. The corrosion potential and corrosion current were determined by scanning voltammetry. An Al 7075-T73 aluminum alloy specimen was suspended in the test solution. The electrical circuit was completed using a platinum screen counter-electrode and a silver/silver chloride reference electrode.

The corrosion parameters were determined by scanning first 250 mV in the anodic direction, then 250 mV in the cathodic direction, from the open-circuit potential of the aluminum alloy. The corrosion potential and current were determined by the intersection of the Tafel slopes for the anodic and cathodic curves.

Two methods were used to prepare coated samples for evaluation. The first method was a conventional formulation of the inhibitor in the epoxy-polyamide primer. The second method was by direct spraying of the inhibitor on the alloy substrate, followed by an epoxy top-coat.

F. RESULTS

Among the nonchromate quaternary ammonium salts (nitrate, phosphate, borate, and molybdate) tested as possible replacements for the strontium chromate corrosion inhibitor used in paint primers for aluminum, the molybdate salt (Q-Mo) was superior in every regard, producing results equivalent to MIL-P-23377, Epoxy Primer Coatings.

The commercially developed molybdate salt corrosion inhibitor (Q-Mo) is a high-purity quaternary ammonium salt, containing less than 1,000 ppm sulfate and 100 ppm chloride. Optimization of the molybdate in epoxy-polyamide primer was successful in achieving the corrosion resistance, fluid resistance, and physical and working properties required. The resistance properties evaluated included hydraulic fluid, lubricating oil, water, and solvent (methyl ethyl ketone). The Q-Mo salt achieved passing grades in all the tests at 3-percent loading. The coatings passed the specification 1,000-hour filiform test and a 2,000-hour exposure in Pacific Ocean salt spray (fog) in the ASTM B-117 test system.

G. CONCLUSIONS

The mechanism of corrosion inhibition is related to dissociation of the quaternary salt in salt water, releasing the ammonium dimolybdate anion and the quaternary ammonium cation. This occurs

when seawater diffuses through the epoxy coating that contains the inhibitor and carries the inhibitor ions with it to the metal-epoxy interface. The inhibition mechanism involves electrochemical polarization of the cathodic sites at the metal-paint interface to retard the evolution of hydrogen and prevent the spread of corrosion under the paint film. In this process, the inhibitor anion is reduced and forms lower-oxidation-state Mo precipitates. These serve as barriers to the principal corrosive agents. The Q-Mo salt was found to dissociate almost three times faster, as tested in a shaking system, in Pacific Ocean water than in an equivalent sodium chloride solution. Thus, seawater (the real-world environment) was used instead of the usual sodium chloride spray (fog), in the B-117 apparatus for the salt corrosion resistance test.

H. RECOMMENDATIONS

A demonstration program is recommended to formulate gallon quantities of the epoxy-polyamide coatings. The coatings will be formulated in exempt solvents and in similar systems that produce water-reducible paints. The solubility studies performed during this program have shown that these coatings are indeed feasible. Application on Air Force flight and ground equipment will then follow.

I. APPLICATION

The sprayable paint system formulated with the nonchromate corrosion inhibitor, quaternary ammonium dimolybdate, can be generally applied to Air Force flight and ground equipment.

J. BENEFITS

The most important long-term benefit that can be derived from the use of the nonchromate corrosion inhibitor is the total elimination of adverse environmental and health hazards and damage caused by conventional chromate-based corrosion inhibitors.

K. TRANSFERABILITY OF TECHNOLOGY

The potential non-DoD users of this technology include shipbuilders and industries related to infrastructure maintenance, such as engineering and maintenance firms for highways and bridges.

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SECTION I

INTRODUCTION

A. OBJECTIVE

The primary objective of the program was to replace inorganic strontium chromate as a corrosion inhibitor in primers and coatings of interest to the Air Force and to prove the efficacy of the replacement inhibitors selected in MIL-P-23377 epoxy-polyamide primer. It was required that the replacement cause minimal change in the physical, anticorrosive, and working properties of the primer, and that it be commercially available or well under way in development.

B. BACKGROUND

The toxic and hazardous characteristics of chromates and Cr(VI) chemicals have been recognized for many years. However, in 1984 the EPA published a document, *Health Assessment Document for Chromium*, which emphasized the significance of these hazards regarding carcinogenicity, mutagenicity, and toxicity (Reference 1). As a result, an increasing number of substitutes have been investigated and tested summarily in an effort to remove, as much as possible, all chromates from the marketplace. Over the past 20 years, many investigations have been performed involving the substitution of water-soluble hydrophilic anions for chromates in coolants and cooling towers (References 2 and 3). When a corrosion inhibitor is intended for dissolution in a conventional oil-base paint medium, the inhibitor must be organophilic, in contrast to the materials used in the cooling towers.

The inhibitors chosen for evaluation in this program were taken from the family of quaternary ammonium salts that contain a single methyl group and three linear, saturated, C₈-C₁₀, alkyl groups directly attached to the nitrogen atom. These compounds—with the appropriate anionic groups—are essentially insoluble in deionized or distilled water, but dissociate readily in a seawater environment. They are otherwise readily soluble in most common paint solvents.

Historically, "quaternized" amines have been used as corrosion inhibitors for oil and gas production (Reference 4). These salts are made up of three methyl groups and a single fatty acid R group, thereby conferring the moderate degree of water solubility/dispersibility required for these applications. The first organophilic monomethyl trialkyl quaternary ammonium dichromate salt was prepared by Hutchins (Reference 5), who reacted a commercial mixture of methyl trialkyl (C₈-C₁₀) ammonium chloride in benzene via double-exchange (phase-transfer reaction) with an aqueous solution of potassium dichromate. The resultant inhibitor, $[\text{CH}_3(\text{C}_8\text{-C}_{10})_3\text{N}]_2 \cdot \text{Cr}_2\text{O}_7$, was

investigated by Clark (Reference 6) and evaluated by Agarwala (Reference 7) in the form of a quaternary ammonium dichromate mixed with other salts for application to high-strength steel and aluminum alloys. Nonchromate investigations were carried out by Khobaib, who studied water-based inhibitors for washing aircraft (Reference 8), and Cabasso, who studied the microencapsulation of nonchromate aqueous inhibitors (Reference 9).

C. APPROACH

Overall, four quaternary ammonium salts, including variations, were selected and tested on this program. Testing involved (1) initial electrochemical evaluation of only the anions in aqueous media, (2) direct deposition of the quaternary ammonium salts on aluminum alloy surfaces, followed by topcoating with epoxy-polyamide and exposure to an ASTM B-117 salt spray, and (3) formulating the quaternary salts in a MIL-P-23377 primer, followed by testing according to specification and to a Pacific-Ocean-water-modified B-117 environment.

SECTION II

MATERIALS

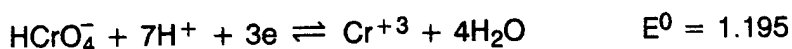
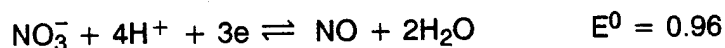
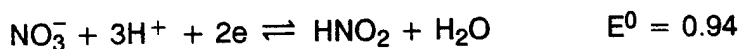
This section describes the quaternary ammonium salt inhibitors evaluated and the primer systems used for the evaluations.

A. INHIBITOR CANDIDATES

Four quaternary ammonium salts were chosen for evaluation: nitrate, phosphate, borate, and molybdate. There was an initial presumption that, barring interaction with the components of the epoxy-polyamide formulation, the candidates would be used directly in the primer. Microencapsulation would be considered only when reactions occurred. A shell would then be applied by an encapsulation process to prevent the reactions. Toward the end of the program, microencapsulation was dismissed as an impracticable device.

1. Quaternary Ammonium Nitrate

References 3, 10, 11, and 12 describe the inhibitory effects of nitrate anion in the presence of chloride in aqueous media, in which the nitrate anion presumably functions as a pacifier and oxidizer similar to Cr(VI) (Reference 13). The reduction potentials, E^0 (in volts versus a standard hydrogen electrode), as shown below, indicate the similarity of the two inhibitors.



Reference 14 (also see Reference 10) lists anions in dilute chloride solutions that act as pitting inhibitors by shifting the critical pitting potential to more noble values: nitrate > chromate > acetate > benzoate > sulfate, in decreasing order of effectiveness. Multiple evaluations were considered appropriate to prove the validity of corrosion inhibition by quaternary ammonium nitrate salts in a primer or paint formulation.

Two suppliers were retained initially to develop the quaternary ammonium nitrate salts: Sherex Chemical Co., Columbus, Ohio, and Henkel Corp., Chicago, Illinois.

a. Sherex EP SC-150-165

The product designation for the quaternary ammonium nitrate, EP SC-150-165, applies to a new process proprietary to Sherex. Analytical data were obtained from a 100-gram

laboratory trial sample prepared for the initial evaluation. A 1-kg bench-scale lot was prepared next. Data for the two materials are given below.

	<u>Laboratory Sample No. 303-125</u>	<u>Kilogram Lot No. 303-187</u>	<u>LMSC Analytical Method</u>
% NO ₃ ⁻	12.8	11.9	Ion chromatography (IC)
% NO ₂ ⁻	< 0.05	< 0.9	IC
ppm Cl	82	<17	Dohrmann microcoulometry
% SO ₄ ²⁻	< 0.1	< 0.008	Digestion, then IC

Based on an empirical gram formula weight (GFW) of 458.5 for CH₃(C₈-C₁₀)₃N · NO₃, of which CH₃(C₈-C₁₀)₃N was 396.5, the percent conversions from the new Sherex process are calculated below:

$$\% \text{ NO}_3 = 100 \times [\text{NO}_3 / \text{CH}_3(\text{C}_8\text{-C}_{10})_3\text{N} \cdot \text{NO}_3] = 100 \times (62.00/458.5) = 13.52\%$$

$$\% \text{ Conversion, No. 303-125,} = (12.8/13.5) \times 100 = 94.8\% \\ \text{(laboratory sample)}$$

$$\% \text{ Conversion, No. 303-187,} = (11.9/13.5) \times 100 = 88.1\% \\ \text{(kilogram bench-scale lot)}$$

The original process, based on Reference 6, lot 213-23, carried out by Sherex, was by a double-exchange phase-transfer reaction of high-purity sodium nitrate with Sherex "Adogen 464," CH₃(C₈-C₁₀)₃N · Cl, in a heterogeneous aqueous-organic solvent mixture. The product from this process contained 9.67 percent NO₃, implying a yield of 71.6 percent. The remaining 28.4 percent of the quaternary was unreacted starting material. The new proprietary process is considered a significant improvement.

b. Henkel Aliquat 336N

The trade name for the Henkel salt is Aliquat 336N. According to a Henkel technical bulletin, it is made by methylation of a straight-chain, saturated, symmetrical tertiary amine (R₃N), Henkel Alamine 336, in which R is a mixture of C₈ and C₁₀ aliphatic chains, with C₈ predominating. It is essentially equivalent, except for its somewhat lower molecular weight, to the Sherex salt.

Analysis of the Aliquat 336N indicated significant residues of halide, equivalent to 2480 ppm Cl, via Dohrmann microcoulometry. When the commodity was dissolved in methyl ethyl

ketone during paint formulations, a white precipitate formed, which was NH_4Cl . When the precipitate was removed, a repeat analysis gave 950 ppm Cl. Both as-received and purified materials were evaluated in the inhibitor tests.

Analysis of Alamine 336, the tertiary amine precursor to 336N, showed less than 10 ppm chloride. When mixed with the quaternary ammonium salt, the amine served as a pH modifier maintaining pH above 4 and below 8.

2. Quaternary Ammonium Hydrogen Phosphate, Sherex EP SC-303-113

The use of HPO_4^{2-} as an inhibitor is discussed in Reference 3. Its application in buffers is well known. Sherex EP SC-303-113, $[\text{CH}_3(\text{C}_8\text{-C}_{10})_3\text{N}]_2 \cdot \text{HPO}_4$, was prepared according to a proprietary process. LMSC analysis gave the following results:

	<u>First Batch</u> <u>(no number)</u>	<u>Second Batch</u> <u>No. 303-149</u>
% HPO_4	12.33	8.2
% SO_4	< 0.1	0.2
% NO_3	< 0.05	< 0.05
% NO_2	< 0.05	< 0.05
% halide	1-2	None detected
ppm Cl	< 500	105

The first batch was discarded because of the presence of the halide used by the manufacturers in their process. The second batch yielded the data as presented.

Based on a GFW of 889 for diquaternary phosphate No. 303-149, the yield was 75.9 percent. To determine the pH of a 20-percent mixture of quaternary salt in ocean water, a well-mixed dispersion was tested after 1 hour of moderate stirring. The pH value was 7.37.

3. Quaternary Ammonium Borate

a. Sherex EP SC-303-60

Borates are also well-known buffers and pH modifiers. EP SC-303-60 is the designation for Sherex's proprietary quaternary ammonium borate. In contrast to phosphates, borates do not generally react with aluminum to form completely insoluble barrier coatings. However, a trace of boric acid as an impurity is not as damaging a corrosive as phosphoric acid. The Sherex sample gave the following results:

% B	1.37	Inductively coupled plasma
ppm SO ₄	14	Inductively coupled plasma
ppm Cl	76	Dohrmann microcoulometry

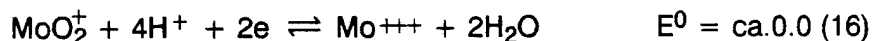
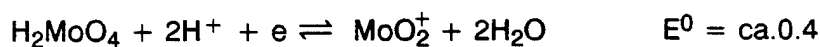
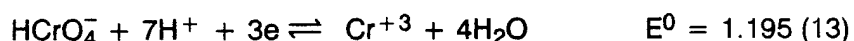
The Sherex borate dissolved rapidly in deionized water, resulting in its elimination as a practical paint candidate, because dissolution of the inhibitor must be slow, over months to years.

b. Akzo RD5444A

The borate salt Akzo RD5444A, covered by U.S. Patent 4,401,577, 1983, was applied previously in a multicomponent corrosion inhibitor mixture as a pH modifier (Reference 15). In contrast to the Sherex borate salt, it is insoluble in deionized water and gives an alkaline reaction, pH 11-13, when mixed with seawater, depending on the concentration and extent of mixing. Akzo indicated that the manufacture of RD5444 included a bleaching additive, which is readily oxidized to sulfate. Subsequent analysis of two samples of the commodity by Parr bomb digestion/oxidation followed by ion chromatography gave an average of 6100 ppm SO₄.

4. Quaternary Ammonium Dimolybdate

Molybdates have been used almost routinely as a substitute for chromium (VI) salts. The principal difference electrochemically is a high reduction potential for Cr(VI) and relatively low values for Mo(VI).



The inhibition involves electrochemical polarization of the cathodic sites at the metal-paint interface that retards the evolution of hydrogen and prevents the spread of corrosion (Reference 17).

There have been many developments in which Cr(VI) has been replaced by Mo(VI), motivated by the very low toxicity of molybdenum salts (Reference 18).

a. Sherex EP SC-150-121

Reference 7 describes the initial concept; Reference 15 describes the development of the inhibitor. The quaternary salt, CH₃(C₈-C₁₀)₃N · NH₄Mo₂O₇, was prepared initially by a phase-

change reaction (double exchange) between ammonium dimolybdate and quaternary ammonium methyl sulfate. The methyl salt was used to minimize introduction of chloride. Initial inhibitor work with the molybdenum salt in epoxy-polyamide primer, as described in Section III, used the Sherex salt; the Sherex research and development effort at Columbus had been discontinued since that time.

b. Akzo Acar 92017

Akzo prepared a molybdate quaternary salt, Acar 92017, which was reported to contain a longer chain length. The molecular weight for the starting tertiary amine indicated that the formula for the salt would be approximately $\text{CH}_3(\text{C}_{12}\text{H}_{25})_3\text{N} \cdot \text{NH}_4\text{Mo}_2\text{O}_7$. Although the effect was not immediately apparent, the aqueous dissociation rate in dilute NaCl solution was influenced by the longer length of the 12-carbon groups. The rate was significantly lower in 3.5-percent NaCl solution than in natural Pacific Ocean water. This had a marked, initially unexplained, effect on the new molyquat's inhibitor behavior when formulated in an epoxy-polyamide primer and exposed to an ASTM B-117 5 percent NaCl fog environment. Results of these tests are given in Section III. Data on the molybdenum salts are given in Table 1.

The higher than theoretical percent Mo analyses indicated the possibility of the presence of some unreacted ammonium dimolybdate starting material. As the ammonium salt is soluble in pure water and the quaternary salt is not, leaching experiments were designed to test this explanation. At the same time, experiments were designed to determine the effect, if any, on dissociation in Pacific Ocean water and in 3.5-percent NaCl, the usual concentration for the dissociation tests.

TABLE 1 ANALYSIS OF QUATERNARY AMMONIUM DIMOLYBDATE SALTS.

Lot No.	Mo ^a (percent)	SO ₄ (ppm)	Cl (ppm)
0254-24 (Lab prep)	24.48	6600	14
0254-28 (Bench prep I)	26.72	< 600	< 70
0254-29 (Bench prep II)	26.14	1500	<100
0.254-39 ^b (Kilogram prep)	27.67	53	< 50

a. Theoretical percent Mo = 22.34, based on monoquaternary substitution, GFW 858.94.

b. Contains 3.3 percent toluene.

In these experiments, 10-percent mixtures (10 grams salt, 90 grams H₂O) of the Akzo kilogram preparation, 0254-39, in the respective H₂O media were shaken slowly and continually in polypropylene bottles. Samples were taken at 6 and 23 days for inductively coupled plasma analysis of Mo. The solutions were filtered through a 0.45- μ m Acrodisc filter. Nephelometry (90° light scattering) measurements were also run following centrifugation of the shaken samples.

The high-purity H₂O-quaternary salt system showed marked colloidal (Tyndall) scattering, indicative of dispersion physically of the salt in distilled H₂O. Mo found in the distilled H₂O-only leachate probably resulted, in large part, from the presence of the colloidal particles, rather than from dissolved (NH₄)₂Mo₂O₇. If the diammonium salt were present in the 0254-39 kg lot, it is probable that several thousand ppm would have been found in the high-purity and other waters. This estimate is based on a calculation of 31.9 percent K₂MoO₄ needed as impurity in order to find 27.67 percent analyzed Mo in the quaternary-Mo-salt commodity. Table 2 gives the extraction/dissociation results. Thus it is more likely that the high percent Mo values obtain from some shorter chain lengths of the Akzo salt, probably C₁₀.

TABLE 2 EXTRACTION/DISSOCIATION DATA FOR QUATERNARY AMMONIUM DIMOLYBDATE IN VARIOUS WATERS.

Medium	Mo Found (ppm)		Nephelometer Turbidity
	6 Days	23 Days	23 Days
High-Purity H ₂ O	67	104	High Tyndall effect 27.3 NTU
3.5% NaCl in Distilled H ₂ O	84	117	No visible Tyndall 0.15 (noise level)
Pacific Ocean Water	177	250	No visible Tyndall 0.65 (noise level)

B. PRIMER MATRICES AND TOPCOATS

This subsection describes the coating matrices used for evaluating the quaternary ammonium inhibitor candidates described in Section IIA. Figure 1 illustrates a typical coating cross section as applied on aluminum alloys.

1. Epoxy-Polyamide Primers

The principal resin-catalyst system used for testing the quaternary ammonium salts was the Deft Coatings epoxy-polyamide two-part primer that contained all added pigments, fillers, and solvents, but no strontium chromate corrosion inhibitor. When SrCrO₄ is added, the formulation is controlled by MIL-P-23377. Quart quantities of primer parts A and B (supplied by Deft), to which

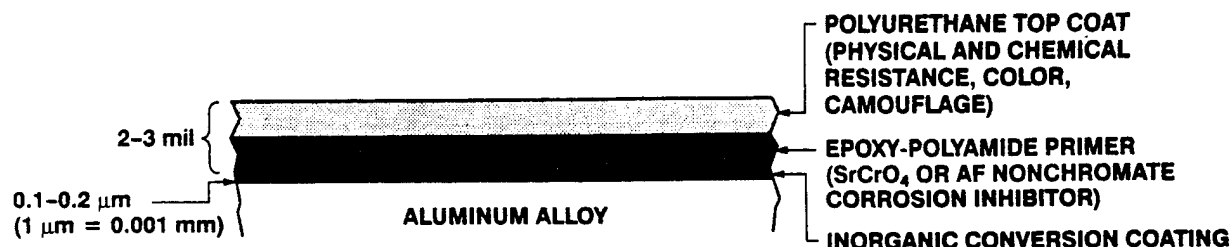


Figure 1 Cross Section of Protective Coatings on Air Force Structural Aluminum Alloys

various loadings of the quaternary ammonium salts were added, were applied to bare and conversion-coated high-strength structural aluminum alloys. The Deft product codes for the formulation, minus SrCrO_4 , is 02W30 resin, part A, and 02W30 CAT, part B. In a few instances, formulations minus all fillers were used. These are product-coded 02X009, part A, and 02X009 CAT, part B. The MIL-P-23377 SrCrO_4 primer used as control is coded 02Y024, part A, and 02Y024 CAT, part B. Formulation of the quaternary salts with the 02W30 and 02X009 coatings requires (1) density of the respective parts A and B and (2) weight percent solids for both parts, calculations of which are given in Appendix A.

The principal test for compatibility was the addition of a candidate quaternary salt to part A and/or part B, separately, followed by combining the two parts and observing any significant changes in viscosity, overnight, relative to parts A and B, mixed, serving as control. In general, addition of the quaternary ammonium salts to the part A resin component resulted in little or no interaction with the hydroxy groups on the Bisphenol A, diglycidyl ether resin. However, there were some reactions with the part B catalysts, which are described in specific cases in Section III.

2. Self-Priming Topcoat and Microencapsulation

This relatively new two-part coating formulation "Unicoat" requires no separate primer between aluminum conversion coating and polyurethane topcoat (Reference 19). Quaternary molybdate salts were added to part A, polyester polyol resin, and part B, hexamethylene diisocyanate, as separate liquids, and mixed. In no case was the addition without marked effect; i.e., rapid coagulation of the components occurred within minutes, precluding the use of the quaternary salts in either of the two components. The intent was to substitute the solvent-soluble molybdate quaternary for the inorganic zinc molybdate solids originally formulated. A low percentage of quaternary salt dissolved in the system would have a minimum effect on the flexibility of the coating. TT-P-2756, 24 September 1990, *Self-Priming Topcoat*, is the controlling document.

The conventional response to these interactions is to microencapsulate the liquid in a solvent-resistant shell. The real-world problem is that no shell material is completely impermeable to any solvent for periods necessary to warrant stability in the paint can. Add to this the need to reformulate when the microcapsules (now nonreactive) are mixed into either part and the need to have no solvent present in that part. Other problems are related to the amount of inhibitor core (payload) that can be microencapsulated while at the same time preventing the core inhibitor from depositing within or on the shell during oil-in-water microemulsification processing. Reference 20 describes compromises and solutions to this problem that were required in a related program.

SECTION III

TEST AND EVALUATION OF CORROSION INHIBITORS

Electrochemical corrosion and coating evaluations were the principal methods used to evaluate the quaternary ammonium salt inhibitors. The electrochemical evaluations involve the anions only, whereas the panel tests include the complete molecule.

A. ELECTROCHEMICAL CORROSION SCREENING TESTS

Corrosion screening tests were performed on solutions containing 3.5-percent sodium chloride with 500 ppm of the specified inhibitor added as the sodium salt, i.e., sodium chromate, sodium molybdate, etc. The corrosion test was performed according to ASTM G3-89, whereby the corrosion potential and corrosion current are determined by scanning voltammetry. An Al 7075-T73 aluminum alloy specimen was suspended in a container of the solution of interest. The electrical circuit was completed using a platinum screen counter electrode and a silver/silver-chloride reference electrode. The corrosion parameters were determined by scanning first 250 mV in the anodic direction, then 250 mV in the cathodic direction, from the open-circuit potential of the aluminum alloy as measured against the silver/silver chloride reference electrode. The corrosion potential and current were determined by the intersection of the Tafel slopes (least squares fit) for the anodic and cathodic curves.

Figures 2 and 3 detail the results of the corrosion studies. The anodic Tafel slope is shown for each of the solutions studied in the preliminary electrochemical scan of the inhibitor candidates. The Tafel slope indicates the propensity to corrode in an electrochemical environment. The chromates have the lowest Tafel slope and thus have the highest inhibitor action in the 3.5-percent NaCl solution. Molybdates also indicate inhibitor properties, while nitrates and phosphates both appear to speed up the corrosion process.

The nitrate results appear at variance with the conclusions derived in References 3, 10, 11, and 12. Nevertheless, the tests of the slowly soluble, hydrophobic quaternary salts – which could not be tested directly in the aqueous medium – were continued, with emphasis placed on evaluating the quaternary salts in epoxy primers.

The studies were performed using a Solartron Model 1266 Electrochemical Interface, which was computer controlled (IBM-AT clone) using DC-CorrWare developed by Scribner Associates. This software performed the corrosion measurements and plotted the Tafel slopes shown in the figures.

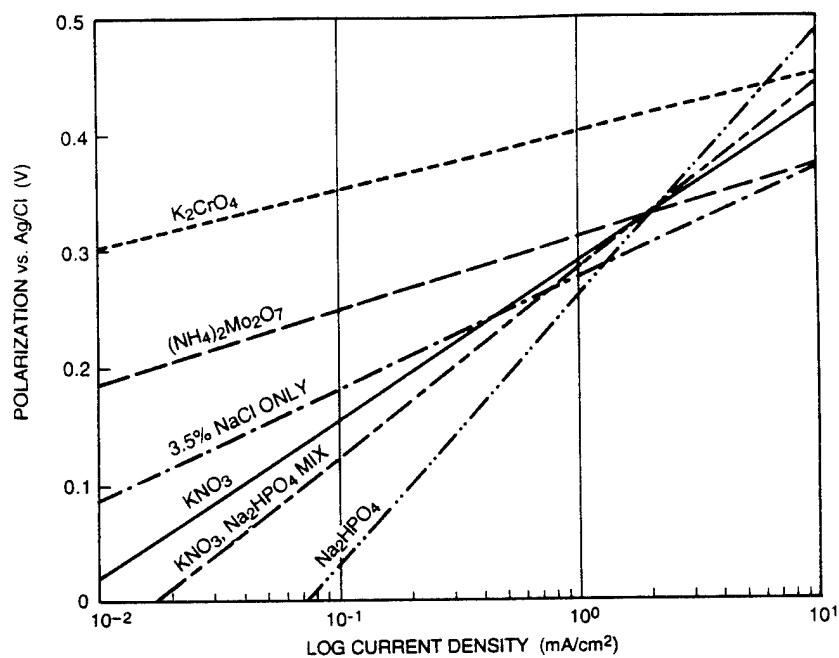


Figure 2 Inhibitor Study of Selected Anions in 3.5-Percent NaCl, pH 6, on 7075-T73 Alloy [500 ppm Inhibitor]

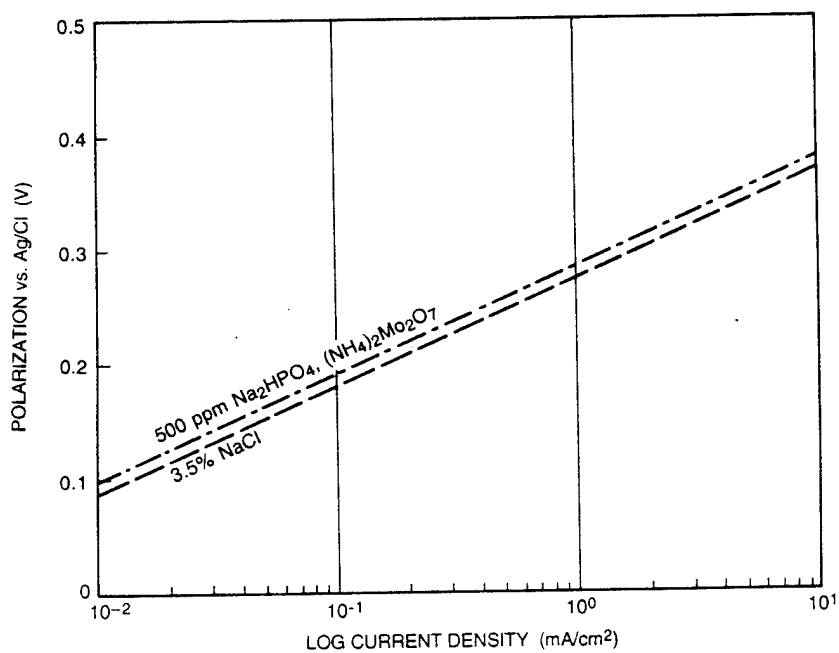


Figure 3 Inhibitor Study of Mixed Dimolybdate and Monohydrogen Phosphate Anions in 3.5-Percent NaCl, pH 6, on 7075-T73 Alloy

B. EPOXY-POLYAMIDE COATINGS

In this section, the evaluations are presented in the same order as they were performed during the course of the program. Two methods were used: (1) conventional formulation of the inhibitor in the primer, which was the principal means of evaluation, and (2) direct coating of the inhibitor on the alloy substrate by spray from a solvent solution, followed by top coating with epoxy. The second procedure allowed evaluation of the inhibitors without the need to optimize formulations, a significant time saving. The calculated weight of inhibitor was based on an amount, weight for weight, that would take the place of the strontium chromate in the MIL-P-23377 epoxy-polyamide primer. For a 3×5-inch panel, 0.2–0.3 grams of quaternary ammonium salt was deposited from a toluene solution. A disadvantage of the procedure is that some bleed-through or surface inhomogeneity occurs because of inhibitor solubility in the epoxy during cure. The coatings were scribed (cross-hatched) according to ASTM D-1654, unless otherwise noted. Before coating via spray, the panels were mechanically deoxidized with 3M Scotch-Brite VF pads (alumina-impregnated nylon web), then solvent cleaned using wet Rymple cloth (metal-finishing grade "cheese" cloth) to remove the residual aluminum abrasion products.

1. Formulation and Test Series 1

- Quaternary ammonium salts: phosphate, nitrate
- Epoxy-polyamide: 02X009, clear epoxy topcoat
- Substrates: Al 7075-T6 and 7075-T73 high-strength structural-alloy panels

The two quaternary ammonium nitrates evaluated were laboratory preparations. Lot 303-125, labelled Sherex Nitrate II, was made by the Sherex proprietary process. Lot 213-23 was prepared using the original double-exchange, phase-transfer process that had left 0.6 percent Cl in the end product. When combined, the phosphate and nitrates were mixed equally by weight to give approximately 0.3 gram per panel. The two tempers of the 7075 Al alloy were used to distinguish between different modes of corrosion: T73, pitting; and T6, general and exfoliative corrosion. Table 3 gives the corrosion data obtained over a 1000-hour (6-week) period.

Overall, the Sherex II and Henkel nitrates yielded inconsistent improvements over the clear, unfilled epoxy. The phosphate and mixed phosphate-nitrates failed. Either small amounts of phosphoric acid were being produced by hydrolysis, or some impurities had been introduced in the manufacturing process. Nevertheless, it was considered appropriate to continue the inhibitor tests and the sample analyses.

TABLE 3 TEST NO. 1—ASTM B-117 CORROSION RESISTANCE OF QUATERNARY AMMONIUM NITRATE AND PHOSPHATE SALTS DIRECT ON ALLOY SUBSTRATE.

Panel	Coating or Inhibitor	Scribe Marks	Observations					
			1	2	3	4	5	6 wks (1000 h)
7075-T73 3 in. × 5 in. × 40 mil (No. of panels)	All panels topcoated with Clear Epoxy							
	None, Clear Epoxy	No						
	None, Clear Epoxy	Yes			■ ^a	(pitting at X)		
	SrCrO ₄ , MIL-P-23377 Coating	No						
	SrCrO ₄ , MIL-P-23377 Coating	Yes						
	Sherex Phosphate	No			■	(corrosion under film)		
	Sherex Phosphate	Yes		■	(lifting at X)			
	Sherex Nitrate II, 303-125	No			■	(pitting under film)		
	Sherex Nitrate I, 213-23	No			■	(pitting under film)		
	Henkel Nitrate	No						
	Henkel Nitrate	Yes			■	(blisters)		
	Mixed Sherex Nitrate II and Phosphate	No	■	(pitting through film, similar to acid etch)				
	Mixed Henkel Nitrate and Sherex Phosphate	No	■	(pitting through film)				
7075-T6 3 in. × 5 in. × 32 mil (No. of panels)	None, Clear Epoxy	No						
	None, Clear Epoxy	Yes			■	(lifting at X)		
	SrCrO ₄ , MIL-P-23377 Coating	No						
	SrCrO ₄ , MIL-P-23377 Coating	Yes						
	Sherex Phosphate	No		■	(pitting through film)			
	Sherex Nitrate II	No						
	Sherex Nitrate I	No			■	(corrosion under film)		
	Henkel Nitrate	No			■	(lifting at X)		
	Henkel Nitrate	Yes						
	Sherex Nitrate II and Phosphate	No	■	(extensive pitting)				
	Henkel Nitrate and Sherex Phosphate	No	■	(extensive pitting)				

^a ■ Indicates panels removed because of corrosion failure.

2. Formulation and Test Series 2

- Quaternary ammonium salts: nitrate, borate, and tertiary amine
- Epoxy-polyamide: 02W30, filled, as topcoat (no SrCrO_4), and as formulation base
- Substrates: Al 7075-T6

This series used the Henkel quaternary ammonium nitrate and Henkel tertiary amine ($\text{C}_{12}\text{H}_{25}\text{N}$). Akzo borate and the Henkel amine were added to adjust the pH values of the Henkel nitrate to 7-8. Both direct spray-on and paint formulations were tested in this series (see Table 4). Additions of amine or borate provided no advantage, but the Henkel nitrate appeared to improve the salt-spray resistance in both direct-on and 9 percent nitrate additions. The Henkel nitrate was purified by diluting with methyl ethyl ketone or toluene to remove the NH_4Cl . The 9 percent addition, however, resulted in a slow (poor) time to set.

3. Formulation and Test Series 3 and 4

- Quaternary ammonium salts: nitrate, borate
- Epoxy-polyamide: 02W30, filled, as topcoat (no SrCrO_4), and as formulation base
- Substrate: Al 7075-T6

Chemical analysis of the initial batch of quaternary ammonium phosphate disclosed the presence of an extraneous halide included in the process by the manufacturer. Sherex prepared a second batch without the additive. Samples were mixed with Sherex nitrate salt II. Salt-spray tests of direct-on depositions of the mixtures and formulation of the mixtures in epoxy-polyamide resulted in 1-2 week failures of every formulation. Corrosion was attributed to excess sulfate in the phosphate quaternary. Borates were then added as a replacement for phosphate, but the failures continued. Analysis of the RD5444A borate showed 6100 ppm sulfate (derived from a sulfite bleachant in the borate commodity). The sulfate in the nitrate-borate test mixture was probably caused by oxidation of sulfite by the nitrate quaternary salt, with concomitant corrosion caused by the high level of sulfate anion.

4. Formulation and Test Series 5 and 6

- Quaternary ammonium salts: nitrate, borate
- Epoxy-polyamide: 02W30 filled topcoat and formulation base (no SrCrO_4)
- Panels: 7075-T6 and 2024-T3, both Alodine 600 and 1200 conversion coated

A kilogram batch of quaternary ammonium nitrate was prepared by Sherex for further evaluation. A small amount of borate (2 percent by weight of the quaternary nitrate) was added to

TABLE 4 TEST NO. 2—ASTM B-117 CORROSION RESISTANCE OF QUATERNARY AMMONIUM NITRATE, BORATE, AND TERTIARY AMINE DIRECT ON ALLOY SUBSTRATE AND IN EPOXY-POLYAMIDE FORMULATIONS.

Panel ^a	Coating or Inhibitor	Additive	Observations					
			1	2	3	4	5	6 wks (1000 h)
7075-T6 3 in. x 5 in. x 32 mil (No. of panels)	Panels topcoated with 02W30							
(7)	<u>Direct-On</u> Henkel Nitrate ^b	None				■ ^d		
(4)	Henkel Nitrate	0.1 Amine				■		
(6)	Henkel Nitrate	0.1 Borate			■			
(7)	Henkel Nitrate	NH ₄ Cl removed			■			
(5)	02W30 Epoxy	None	■					
(4)	<u>Formulations</u> 7% Henkel Nitrate ^c	None	■					
(4)	7% Henkel Nitrate	0.1 Amine	■	■				
(5)	7% Henkel Nitrate	0.1 Borate	■					
(4)	9% Henkel Nitrate	None			■			
(4)	9% Henkel Nitrate	0.1 Amine			■			
(4)	9% Henkel Nitrate	0.1 Borate			■			

^a All panels scribed.

^b Quaternary salts added after 1/2 h epoxy-polyamide induction period.

^c Nitrate quaternaries purified before adding to formulation.

^d ■ Indicates panels removed because of corrosion failure.

adjust the pH to 7.6–7.7. In this way, the amount of sulfate in the mixture was minimized, estimated at < 0.02 percent. The inhibitors were added direct-on to 7075-T6 panels, and equivalent formulations were prepared with Deft 02W30 epoxy-polyamide. Nevertheless, acceptable corrosion inhibition was not achieved, as measured by either application technique. Four of five test panels of each set failed near 500 hours, significantly less than MIL-P-23377 SrCrO_4 primer panels, all of which remained unchanged at 1000 hours.

Another test series was run concurrently. It used Alodine 600 and 1200 chromate conversion-coated substrates, 7075-T6 and 2024-T3, as prescribed in MIL-P-23377. The same kilogram lot of quaternary ammonium nitrate plus 2 percent borate was used as previously. Although overall pitting and blistering corrosion were held back several weeks, this was attributed principally to the presence of the chromate coatings, rather than the nitrate or nitrate-borate mixtures. The nitrate quaternary salt, but not the mixture, showed improvements in corrosion resistance, but not enough improvement to qualify it as a replacement for SrCrO_4 .

At this point, it became apparent that the nitrate quaternary was oxidizing the hydroxyl groups of the part A epoxy resin component. An alternative explanation considered was that the nitrate quaternary oxidized the hydroxyl groups in the MIL-T-81772 epoxy diluent and/or the part B catalyst solvents used in the epoxy-polyamide two-part system. If so, the nitrate quaternary salt would need to be microencapsulated. Before proceeding further, we decided to evaluate the quaternary ammonium dimolybdate salt, which might not need the encapsulation process.

5. Formulation and Test Series 7

- Quaternary ammonium salt: dimolybdate, borate
- Epoxy-polyamide: 02W30 formulation base (no SrCrO_4)
- Panels: 7075-T6

As a preliminary test, a previously analyzed Sherex molybdate quaternary salt, available in the laboratory, was added at two levels, 5 and 10 percent, based on total coating weight, to MIL-P-23377E minus the SrCrO_4 inhibitor. For the 10 percent level, a separate 1 percent quaternary ammonium borate was added to the dimolybdate to serve as a buffer. The Sherex dimolybdate, numbered 150-151, contained the following impurities: Cl^- 37 ppm, SO_4^{2-} 0.64 percent (Reference 15). Results are given in Table 5. The 10 percent quaternary ammonium dimolybdate (Q-Mo) yielded the longest period of corrosion resistance, up to 1700 hours before blister failures occurred at the scribes of two of three of the panels. Addition of 1 percent borate quaternary resulted in deterioration of the inhibition, thereby confirming the poor utility of the borate salt. The presence of 0.6 percent SO_4 in the Q-Mo salt did not appear to significantly affect the inhibitor activity during the

TABLE 5 TEST NO. 7 --ASTM B-117 CORROSION RESISTANCE OF QUATERNARY AMMONIUM DIMOLYBDATE IN EPOXY-POLYAMIDE FORMULATIONS.

Panel ^a	Inhibitor	Additive	Observations					
			1	2	3	4	5	6 wks (1000 h) ----- > 9 wks (1700 h)
7075-T6 3 in. x 5 in. x 32 mil (No. of panels)	Sherex lab preparation							
(3)	None	None	▲ ^b					
(3)	5% Q-Mo	None			▲			
(3)	10% Q-Mo	None						▲
(3)	10% Q-Mo	1% Q-Borate			▲			

^a All panels scribed.

^b ■ Indicates panels removed because of corrosion failure.

first 1000 hours. The two sets of photos shown in Figure 4 illustrate the corrosion-inhibiting activity of the 10 percent Q-Mo epoxy-polyamide coatings after 1700 hours ASTM B-117 exposure.

6. Formulation and Test Series 8

- Quaternary ammonium salt: dimolybdate
- Epoxy-polyamide: 02W30 formulation base, minus SrCrO_4
- Substrate: 7075-T6 and 7075-T73

This series used the first sample of Q-Mo obtained from Akzo Chemical Co., lab prep 0254-24. Analytical data for the sample are given in Section IIA4, Quaternary Ammonium Dimolybdate. The high level of SO_4^{2-} , 6600 ppm, was noted. The Q-Mo was formulated at 8 and 10 percent, based on total weight of coating solids. Exposures in B-117 salt spray yielded pitting and blister corrosion failures in 72 hours (3 days) at the scribe lines. The high level of sulfate in the inhibitor was the likely cause, and no further formulations were prepared with the sample.

7. Formulation and Test Series 9

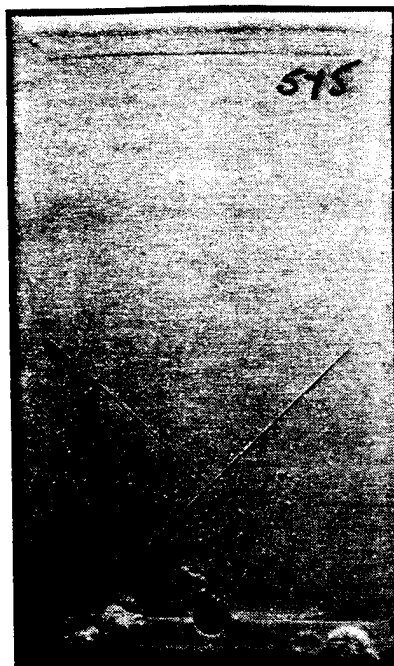
This series was formulated with the moderately-high-purity Akzo 92017 bench preparation I, 0254-28, quaternary ammonium dimolybdate. Three levels were formulated: 6, 8, and 10 percent by weight total solids. The epoxy-polyamide was applied to physically deoxidized, solvent-cleaned samples and cured at room temperature per MIL-P-23377. Salt-spray exposures were carried out according to ASTM B-117. The results, as shown in Table 6, were not positive, in that the exposure caused excess blisters on all panels at less than 1000 hours (840 hours).

Tests began at this time to evaluate the dissociation of the new salt versus the original material prepared by Sherex, which was no longer preparing R&D material at this time. It was hypothesized that the new Q-Mo salts might differ significantly from the original Sherex materials, and therefore the quantity of the molybdate anion released would be significantly lower for the higher molecular weight, less-soluble Akzo quaternary salts. The release experiments detailed in Section IIA4 describe the differences between the dissociations in 3.5-percent NaCl solution and in Pacific Ocean water. It was on this basis that a detailed test was designed to evaluate the Q-Mo filled coatings in both the ASTM B-117 environment and a Pacific Ocean salt-water (fog) spray, using a dedicated salt box for the ocean-spray experiments.

Next, the solubility and compatibility of Q-Mo in paint solvent systems were determined. This information was used for formulating the molybdenum quaternary salt with the part A resin of the two-part epoxy-polyamide. Adding Q-Mo to the part B catalyst resulted in coagulation. This



Before exposure



After 1700-hour exposure



Before exposure



After 1700-hour exposure

Figure 4 Photographs Showing Inhibitor Activity of 10 Percent Quaternary Ammonium Dimolybdate Epoxy-Polyamide Coatings in ASTM B-117 Salt Spray After 1700 hours. The bottom set also contains 1 percent borate quaternary.

TABLE 6 TEST NO. 9—ASTM B-117 CORROSION RESISTANCE OF Q-Mo IN EPOXY-POLYAMIDE FORMULATIONS.

Panel ^a	Inhibitor	Observations					
		1	2	3	4	5	6 wks (1000 h)
7075-T73 3 in. x 5 in. x .40 mil (No. of panels)	ACAR 92017, Prep. 0254-28						
(2)	None	▲ ^b					
(2)	6% Q-Mo	▲					
(2)	8% Q-Mo	▲					
(2)	10% Q-Mo		▲				
		(many blisters at scribe)					
7076-T6 3 in. x 5 in. x .32 mil (No. of panels)							
(2)	None		▲				
(2)	6% Q-Mo					▲	
(2)	8% Q-Mo	▲					

^a All panels scribed.

^b ■ Indicates panels removed because of corrosion failure.

may have been caused by lack of solubility of the Q-Mo in the principal solvents of part B: NBA, NBAI, and IPA, rather than by interaction with the polyamide (amidoamine) catalyst. To test for solubility and compatibility, approximately 100 mg of the Q-Mo salt was mixed for approximately 10 minutes in 15 cm³ of each of the following solvents:

<u>Single Solvents</u>	<u>Solubility</u>
Xylene	Yes
Toluene	Yes
Methyl ethyl ketone (MEK)	Yes
Methyl isobutyl ketone (MIBK)	Yes
<i>n</i> -Butyl acetate (NBA)	Partial (slow)
<i>n</i> -Butyl alcohol (NBAI)	Poor
Isopropyl alcohol (IPA)	Poor
Propylene glycol methyl ether (PGME)	No
Isooctane	No
<u>Paint Solvent Mixtures</u>	
75 PGME/25 xylene (by volume)	No
65 MIBK/35 xylene	Yes
50 Toluene/50 <i>n</i> -Butyl alcohol	Yes (slow)
Epoxy thinner (MIL-T-81772B(2)) [50 MEK, 20 MIBK, 30 PGME]	Yes (slow)
Epoxy resin solvent mixture, Part A [18 toluene, 46 MEK, 18 NBA, 18 lacquer diluent No. 6]	Yes
<u>Epoxy Component Mixtures</u>	
Part A epoxy resin, no fillers	Yes (no incompatibility)
Part A epoxy resin, clay, SiO ₂ , TiO ₂ , but no strontium chromate, SrCrO ₄	Yes (no incompatibility)

A qualitative test was run in which the molybdate salt was dissolved in part A at 10 percent by weight solids based on total coating weight solids. Part B was then added to the mixture, which was mixed and let stand without permitting loss of solvent (airtight coverage with aluminum foil). The presence of the salt was observed to have no effect on pot life/cure time on standing for 2 days versus the A plus B system minus the molybdate salt as control. This implies that the salt can be blended into part A as the corrosion-inhibitor compound, followed by mixing with the part B hardener.

8. Formulation and Test Series 10

a. Salt-Spray Corrosion Resistance: Pacific Ocean Salt Water Versus ASTM B-117 5-Percent NaCl Solution

The 1-kg batch of Acar 92017 quaternary ammonium molybdate salt obtained from Akzo Chemical, lot 0254-39, was received as a light-green waxy solid. Percent solids was 96.7 percent; the residue was 3.3 percent toluene. Based on the significantly lower dissociation rate in 3.5-percent NaCl in deionized water versus Pacific Ocean salt water (see Table 2), it was determined that the Pacific Ocean water would be used as the principal corrosion test medium. The medium was filtered ocean water supplied by Steinhart Aquarium, San Francisco. Approximately 275 gallons were obtained for the 2000-hour (84-day) exposure. Salinity was 30.3 parts per thousand, and pH was 7.62. Pacific Ocean water in the San Francisco area fluctuates between 28 and 32 in salinity, according to the Aquarium technical director. For a comparison of ocean water ion content with sodium chloride solution, Table 7 lists the concentration of the most abundant ions in seawater of 35 percent salinity. For comparison with the results obtained in the ocean water salt-spray fog, panels were also exposed to the usual B-117 system, 5-percent NaCl fog.

TABLE 7 CONCENTRATIONS OF THE MOST ABUNDANT IONS IN SEAWATER OF 35 PERCENT SALINITY (REFERENCE 21).

Density of seawater: 1.023 grams/cm³ at 25°C (75°F)

Ion or Molecule	Concentration	
	(m mol/kg of seawater)	(grams/kg of seawater)
Na ⁺	468.5	10.77
K ⁺	10.21	0.399
Mg ²⁺	53.08	1.290
Ca ²⁺	10.28	0.412
Sr ²⁺	0.09	0.008
Cl ⁻	545.9	19.354
Br ⁻	0.84	0.067
F ⁻	0.07	0.0013
HCO ₃ ⁻	2.30	0.140
SO ₄ ²⁻	28.23	2.712
B(OH) ₃	0.416	0.0257

The Q-Mo salt was formulated at 3, 5, 7, and 9 percent levels based on total weight of the dry coatings. The epoxy-polyamide formulations were deposited on Alodine 1200S, Class 1A, MIL-C-81706, conversion coatings on 2024-T3 aluminum alloy panels. Alclad 2024-T3 panels were used for the filiform corrosion tests. The molybdate was dissolved in part A, but the diluent was 50/50 toluene and methyl isobutyl ketone, instead of the usual MIL-T-81772 thinner that contains a high percentage of oxygenated solvents that do not readily dissolve the Q-Mo salt. In addition to the Pacific Ocean and 5-percent NaCl fog corrosion test results, many properties listed in MIL-P-23377 were evaluated, and are detailed below. Table 8 gives the corrosion results in the standard B-117 environment, and reports the Pacific Ocean fog results for comparison on the same sheet. The differences are significant, and are likely related to the more rapid release of the ammonium dimolybdate anion. It is surmised that the corrosion resistance would be higher for the ocean water exposure (more inhibitor released per unit time) if the salt content were somewhat higher, 3.2-3.6 percent, the usual concentration of salts in open ocean seawater. Figures 5a and b show the corrosion failures for the ocean-water exposure of the control and 3-, 5-, and 7-percent Q-Mo epoxy panels. The successful 3-percent Q-Mo coating system is shown after 2000-hour exposure. Obviously, the ions other than Na^+ and Cl^- in the seawater are the cause of the difference in rate of dissociation. It is speculated that K^+ , Mg^{2+} , Ca^{2+} , and SO_4^{2-} , as well as Br^- , are the ions that influence this difference, but work to support this contention is needed.

Figures 6a and b are the equivalent panels exposed to the ASTM B-117 5-percent NaCl environment. The mechanism of failure, i.e., blistering over the surface of the 7-percent Q-Mo coating, not at the scribe marks, indicates cohesive failure, since an excess of quaternary salt will inhibit crosslinking in the epoxy-polyamide; here the Q-Mo acts as a nonreactive diluent. Other examples are found in the fluid, water-resistance, and adhesion tests described below.

b. Fluid Resistance (Reference MIL-P-23377F, para 3.8.4)

The primer film shall withstand 24-hour immersion in MIL-L-23699 lubricating oil at $121 \pm 3^\circ\text{C}$ and MIL-H-83282 hydraulic fluid at $66 \pm 3^\circ\text{C}$ (using another panel) without showing any softening, blistering, loss of adhesion, etc., 4 hours after removal.

c. Water Resistance and Adhesion (Reference MIL-P-23377F, para 3.8.1 and 3.7.5)

Topcoated (polyurethane MIL-C-83286) primer panels immersed in distilled water for 4 days at $49 \pm 3^\circ\text{C}$ shall show no softening, wrinkling, blistering, loss of adhesion, or any other coating deficiency.

TABLE 8 TEST NO. 10—ASTM B-117 CORROSION RESISTANCE OF KILOGRAM-BATCH Q-Mo IN EPOXY-POLYAMIDE FORMULATIONS AND TEST NO. 11—PACIFIC OCEAN FOG CORROSION RESISTANCE OF KILOGRAM-BATCH Q-Mo IN EPOXY-POLYAMIDE FORMULATIONS.

TEST NO. 10—NaCl

Panel ^a	Inhibitor	Observations											
		1 wk	2	3	4	5	6 wks (1000 h)	7	8	9	10	11	12 wks (2000 h)
2024-T3 3 in. × 6 in. × 20 mil MIL-C-5541, Class 1A Conversion Coating (No. of panels)	ACAR 92017, kilogram, 0254-039												
	None					▲ b							
	3%						▲						
	5%						▲						
	7%												
	9%												

b (blisters at X)
(blisters at X)
(blisters at X)
(blisters in coating; not at X)
(blisters in coating; not at X)

TEST NO. 11—PACIFIC OCEAN FOG

Panel ^a	Inhibitor	Observations											
		1 wk	2	3	4	5	6 wks (1000 h)	7	8	9	10	11	12 wks (2000 h)
2024-T3 3 in. X 6 in. X 20 mil MIL-C-5541, Class 1A Conversion Coating (No. of panels)	ACAR 92017, kilogram, 0254-039												
	None						▲ (blisters at X)						
	3%						▲ (blisters at X)						
	5%						▲ (blisters and lifting at X)						
	7%						▲ (blisters and lifting at X)						
	9%						▲ (blisters and lifting at X)						

(blisters at X)
(blisters at X)
(blisters and lifting at X)
(blisters and lifting at X)

^a All panels scribed.
^b Indicates panels removed because of corrosion failure.

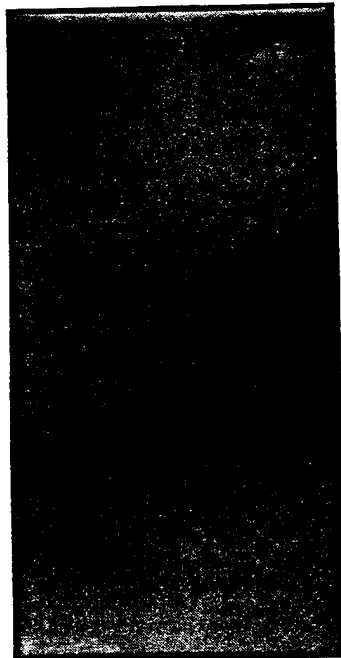
PACIFIC OCEAN WATER



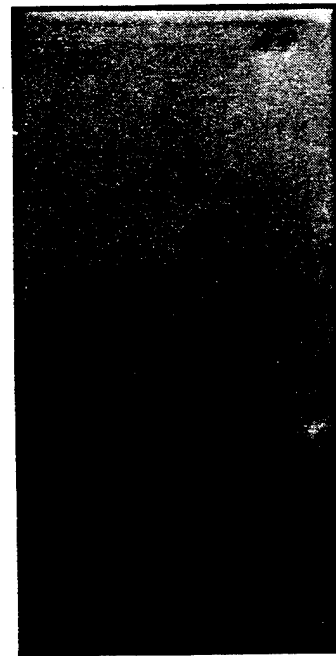
Before salt spray
Control (No Q-Mo)



After 930-hour exposure
Control (No Q-Mo)



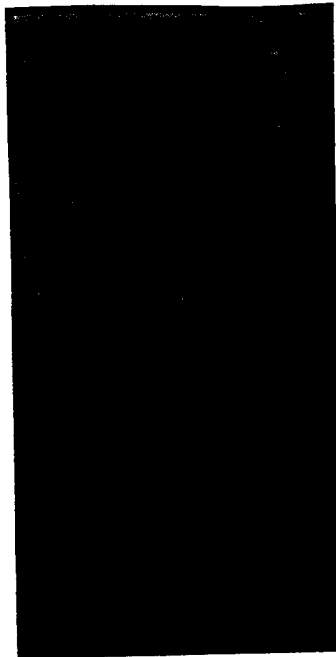
Before salt spray
3% Q-Mo



After 2000-hour exposure
3% Q-Mo

Figure 5a Photographs Showing Inhibitor Activity of Kilogram-Lot Q-Mo in Epoxy-Polyamide Tested in Pacific Ocean Salt Fog (1 of 2)

PACIFIC OCEAN WATER



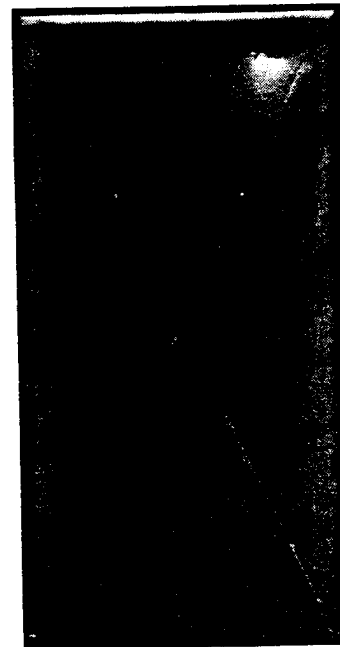
Before salt spray
5% Q-Mo



After 930-hour exposure
5% Q-Mo



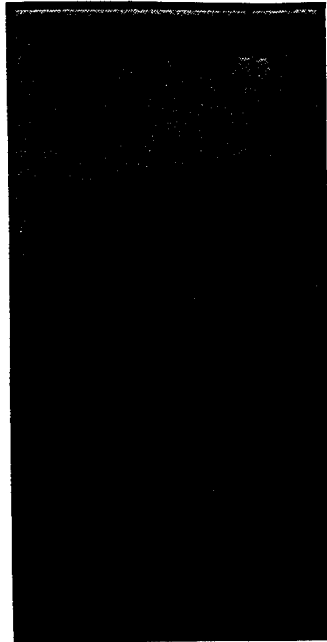
Before salt spray
7% Q-Mo



After 740-hour exposure
7% Q-Mo

Figure 5b Photographs Showing Inhibitor Activity of Kilogram-Lot Q-Mo in Epoxy-Polyamide Tested in Pacific Ocean Salt Fog (2 of 2)

5% NaCl, ASTM B-117



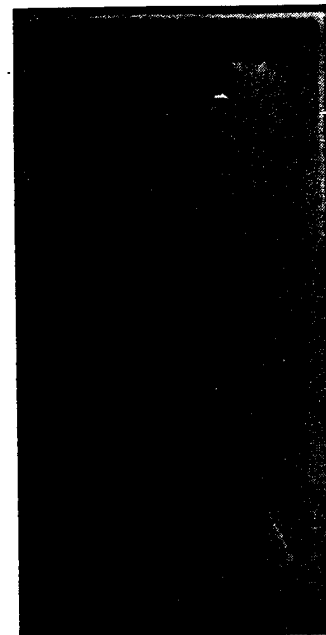
Before salt spray
Control (No Q-Mo)



After 740-hour exposure
Control (No Q-Mo)



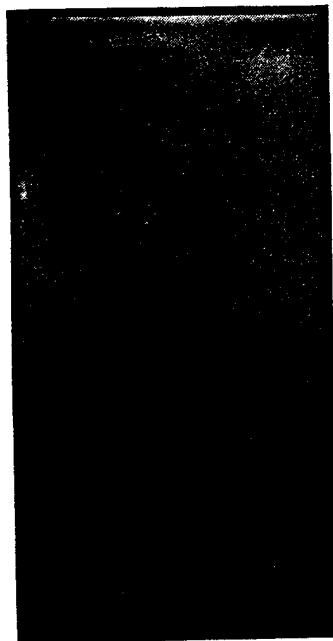
Before salt spray
3% Q-Mo



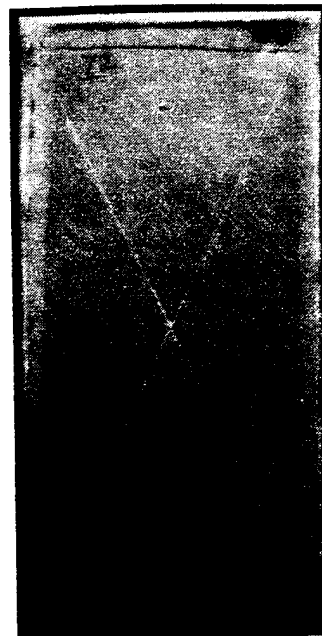
After 930-hour exposure
3% Q-Mo

Figure 6a Photographs Showing Inhibitor Activity of Kilogram-Lot Q-Mo in Epoxy-Polyamide Tested in ASTM B-117 Salt Fog (1 of 2)

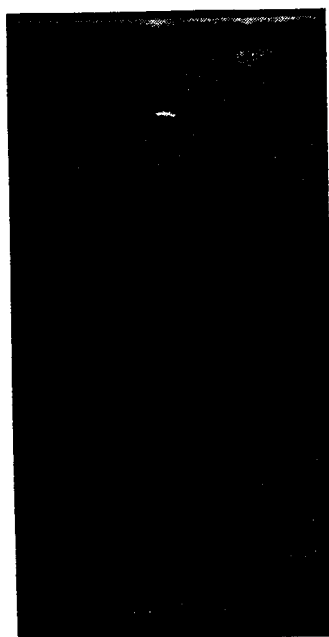
5% NaCl, ASTM B-117



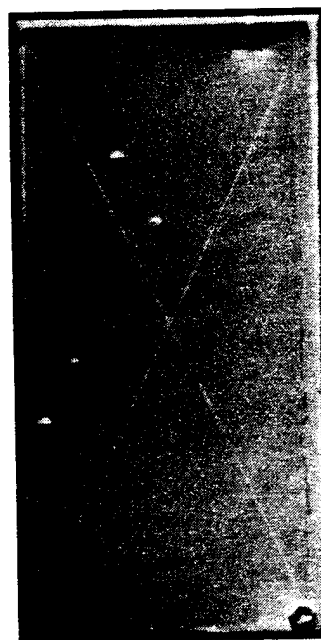
Before salt spray
5% Q-Mo



After 930-hour exposure
5% Q-Mo



Before salt spray
7% Q-Mo



After 336-hour exposure
7% Q-Mo

Figure 6b Photographs Showing Inhibitor Activity of Kilogram-Lot Q-Mo in Epoxy-Polyamide Tested in ASTM B-117 Salt Fog (2 of 2)

d. Solvent Resistance (Reference MIL-P-23377, para 3.8.3)

Wet with methyl ethyl ketone, the primer film must withstand repeated rubbing, 50 passes (25 times rubbed back and forth) over the film with firm finger pressure using a cotton, terry-cloth rag soaked in the solvent.

e. Filiform Corrosion Resistance (Reference MIL-P-23377, para 3.8.2.2)

The primer film is polyurethane topcoated, cured, and scribed diagonally across the surface of the panel to expose the bare substrate. The panels are placed vertically in a desiccator containing 12*N* hydrochloric acid for 1 hour. The panels are then placed, within 5 minutes, in a humidity cabinet at $40 \pm 1.7^{\circ}\text{C}$ and 80 ± 5 percent relative humidity for 1000 hours. Filiform corrosion – which is started purposely by exposure to the HCl corrodent – appears as thread-like filaments initiated from the exposed substrate and spreading under the coating. This corrosion shall extend no more than 1/4 inch from the scribe lines. A majority of the filaments shall be less than 1/8 inch. In Appendix B, photographs of the five panels are shown in Figures B-1 through B-5. Measurements with a steel rule indicated that none of the panels failed the test. Specifically, the 5-, 7-, and 9-percent Q-Mo coatings showed fewer filiform filaments than the zero- and 3-percent Q-Mo coatings. Although the latter panels showed many filaments, no filaments greater than 1/4 inch from the scribe lines were seen. Most were 1/8 inch or less, as accepted by the specification.

Results of the five resistance tests described above are listed in Table 9. Of the coatings evaluated, the 3- and 5-percent Q-Mo panels were the most stable, whereas the 7- and 9-percent Q-Mo panels were poor, i.e., failed in two of the five evaluations.

TABLE 9 FLUID, WATER, SOLVENT RESISTANCE, AND FILIFORM CORROSION TESTING ON Q-Mo EPOXY-POLYAMIDE COATINGS.

Coating	Environment	Results
Control (no Q-Mo)	Hydraulic fluid	Pass
3% Q-Mo	Hydraulic fluid	Pass
5% Q-Mo	Hydraulic fluid	Pass
7% Q-Mo	Hydraulic fluid	Fail, slight loss of adhesion
9% Q-Mo	Hydraulic fluid	Fail, slight blistering
Control (no Q-Mo)	Lubricating oil	Pass
3% Q-Mo	Lubricating oil	Pass
5% Q-Mo	Lubricating oil	Pass
7% Q-Mo	Lubricating oil	Pass
9% Q-Mo	Lubricating oil	Pass
Control (no Q-Mo)	Water	Fail, slight loss of adhesion and softening
3% Q-Mo	Water	Pass
5% Q-Mo	Water	Pass
7% Q-Mo	Water	Fail, slight loss of adhesion and softening
9% Q-Mo	Water	Fail, slight loss of adhesion, softening, and blistering
Control (no Q-Mo)	Solvent, methyl ethyl ketone	Pass
3% Q-Mo	Solvent, methyl ethyl ketone	Pass
5% Q-Mo	Solvent, methyl ethyl ketone	Pass
7% Q-Mo	Solvent, methyl ethyl ketone	Pass
9% Q-Mo	Solvent, methyl ethyl ketone	Pass
Control (no Q-Mo)	Filiform corrosion	Pass
3% Q-Mo	Filiform corrosion	Pass
5% Q-Mo	Filiform corrosion	Pass
7% Q-Mo	Filiform corrosion	Pass
9% Q-Mo	Filiform corrosion	Pass

SECTION IV

RECOMMENDATIONS FOR FUTURE WORK

Based on the development data obtained in this study, a program is recommended to demonstrate the use of the quaternary ammonium dimolybdate inhibitor, Q-Mo, in place of the chromate inhibitor used in current primer systems. To carry this out, the following tasks are given:

1. Scale up the process for synthesizing the dimolybdate salt. Prepare 20 kg in a pilot-scale program.
2. Characterize and determine the limits of yield, impurity content, and other characteristics that will permit preparation of a material and process specification.
3. Formulate the inhibitor in EPA-exempt solvent coatings and paints, and in water-reducible paint systems. (Twenty kg of Q-Mo would be enough to prepare 600 gallons of primer.)
4. Apply and test on major Air Force flight and ground equipment.
5. Prepare specifications for successful coatings.

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APPENDIX A

Q-Mo EPOXY-POLYAMIDE FORMULATION CALCULATIONS AND PROCEDURES

Calculations are given below for the addition of 3-percent Acar 92017, lot 0254-39, to MIL-P-23377 epoxy-polyamide minus SrCrO_4 . The Deft Coatings Co. designation for MIL-P-23377-minus- SrCrO_4 is 02W30. The data used in the calculations are given in Deft Material Safety Data Sheets.

For each 100 cm^3 part A and B to be mixed 1:1 by volume:

$$\begin{aligned} 100 \text{ cm}^3 \text{ part A} \times 1.05 \text{ g/cm}^3, \text{ sp. gr.} &= 105 \text{ g} \\ 49.8\% \text{ solids in A} \times 105 \text{ g} &= \underline{52.29 \text{ g}} \end{aligned}$$

$$\begin{aligned} 100 \text{ cm}^3 \text{ part B} \times 0.839 \text{ g/cm}^3, \text{ sp. gr.} &= 83.9 \text{ g} \\ 22.2\% \text{ solids in B} \times 83.9 \text{ g} &= \underline{18.63 \text{ g}} \end{aligned}$$

In 100 cm^3 A + 100 cm^3 B, there are 52.29 + 18.83 grams, a total of 70.92 grams.

To prepare, for example, a 3-percent Q-Mo formulation based on total solids, solve for X:

$$\begin{aligned} X/(X + 70.92) &= 0.03 \\ X &= 2.19 \text{ grams} \end{aligned}$$

Lot 0254-39 contains 3.3-percent toluene.

$$2.19/0.967 = \underline{2.26 \text{ g Q-Mo}}$$

NOTE: The density of Q-Mo = 1.20 grams/ cm^3 .

Using the calculations, a 20-kg lot of Q-Mo will produce 486 gallons of epoxy-polyamide primer, exclusive of added solvents. To dissolve the inhibitor in part A resin, it is necessary to dilute/let-down the resin system with 50 percent by volume of a 50/50 mixture of methyl ethyl ketone and toluene. With the added diluent, the final volume for the 20-kg production is 606 gallons. The following steps are prescribed for formulation, using 100 cm^3 each of parts A and B:

1. Measure 100 cm^3 of well-shaken (10 min. Red Devil) part A, resin, of Deft Chemical 02W30.

2. Add 50 cm³ of a mixture of 25 cm³ MEK/25 cm³ toluene. Mix until uniform. A magnetic stirrer is satisfactory.
3. Add the preweighed Q-Mo commodity (2.26 grams). Stir. Cover the container with aluminum foil to minimize solvent evaporation. Let stir 1-2 hours. Observe and discontinue when particulates have disappeared.
4. Add 100 cm³ part B catalyst slowly to avoid possible precipitation reactions.
5. Filter through a medium paint-filter (paint or hardware supply). Bottle or cover to prevent evaporation.
6. Use after 1/2-1 hour mixing. Can let stand overnight without increase in viscosity.
7. If necessary dilute further with 50/50 solvent to form an easily sprayed coating.

NOTE 1: It is not necessary to follow the MIL-P-23377 exactly, since the dry coating thickness that is critical to the highly loaded SrCrO₄ system does not apply to the Q-Mo epoxy-polyamide. Using a Binks (Wren) gun, air-brush, B-nozzle, at 24-28 psi, with Ar or N₂ as compressed gas, the formulation produces dry coats 1.0-1.5 mil thick when the wet coating on the test panel becomes opaque in bright light (hood!), i.e., when it hides the aluminum substrate.

NOTE 2: Substitution of Q-Mo, $d = 1.20 \text{ grams/cm}^3$, for SrCrO₄, $d = 3.89 \text{ grams/cm}^3$ produces a lower weight per unit area. The density of the dry SrCrO₄-filled epoxy polyamide is 1.23 grams/cm³, and the density of the dry 02W30 coat (no SrCrO₄) is 1.06 grams/cm³, yielding a 20 percent drop in density. The addition of 3 percent Q-Mo has an almost inconsequential effect on the weight of the new coating. Therefore coatings thicker than the 0.6-0.9 mil SrCrO₄ coating requirement (MIL-P-23377) are acceptable, with current estimates at 1.0-1.5 mils.

APPENDIX B

FILIFORM CORROSION PHOTOGRAPHS OF Q-Mo EPOXY-POLYAMIDE COATINGS

These are photos that illustrate the variety of filiform filaments produced in the MIL-P-23377 environment. There were no failures, including the control, since none of the filaments were over 1/4 inch, and the majority were less than 1/8 inch. The 5-, 7-, and 9-percent Q-Mo coatings showed the least predilection toward filament formation, as can be seen by inspection; and the zero and 3 percent, the most, but passed according to measurement. Figures B-1 through B-5 show the five coatings and associated filaments.

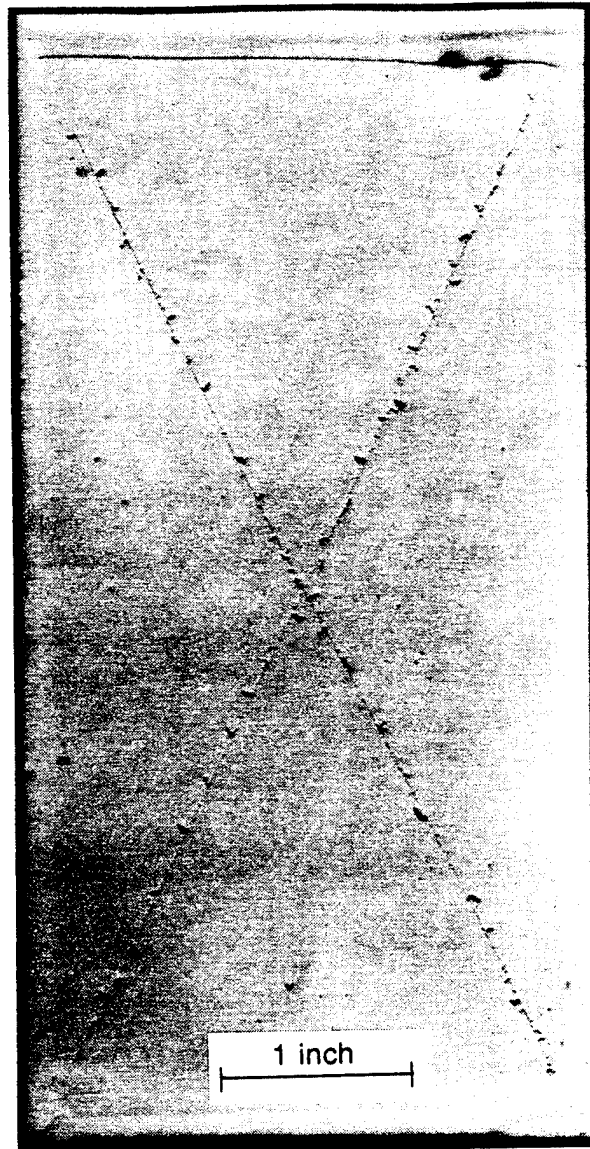


Figure B-1 Photograph of 1000-hour Filiform Corrosion of 0-Percent Q-Mo Epoxy-Polyamide Coating, Panel 83. Pass.

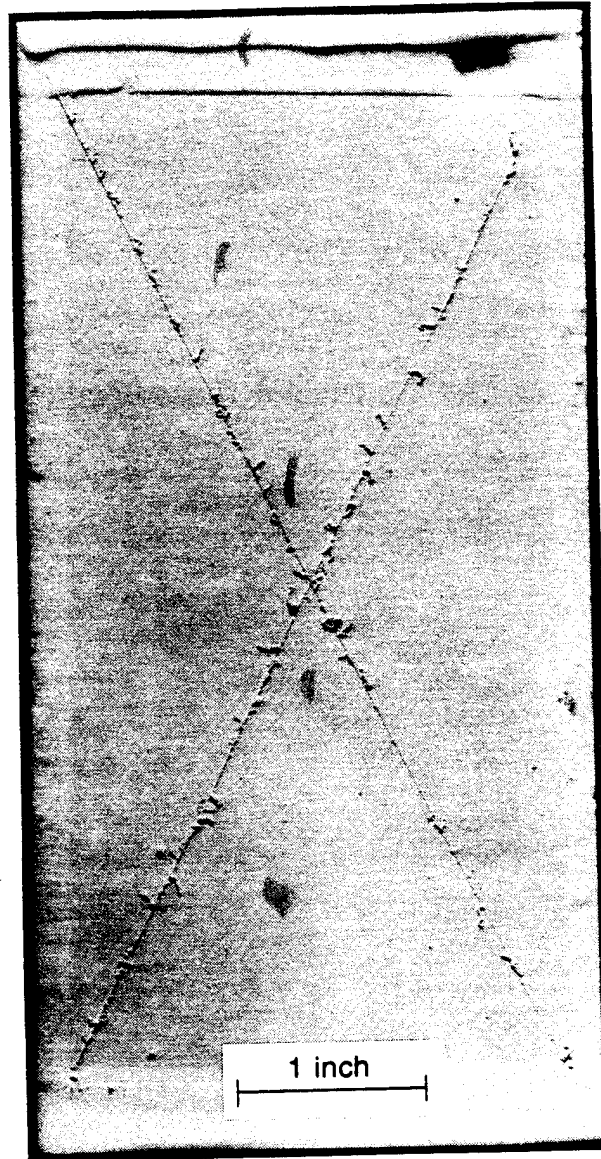


Figure B-2 Photograph of 1000-hour Filiform Corrosion of 3-Percent Q-Mo Epoxy-Polyamide Coating, Panel 90. Pass.

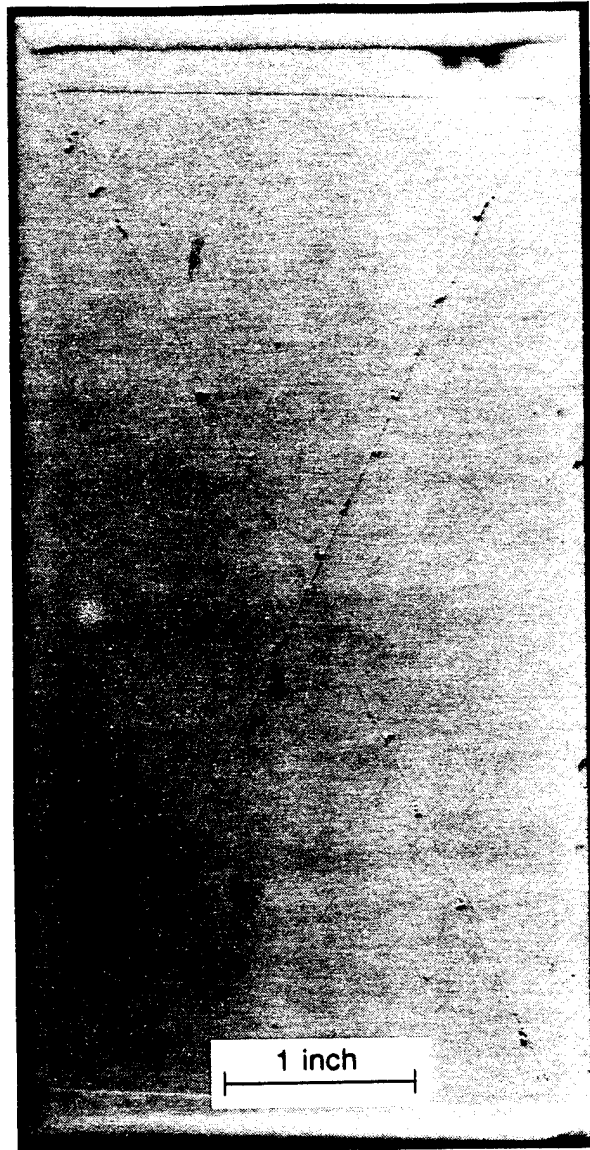


Figure B-3 Photograph of 1000-hour Filiform Corrosion of 5-Percent Q-Mo Epoxy-Polyamide Coating, Panel 93. Pass.

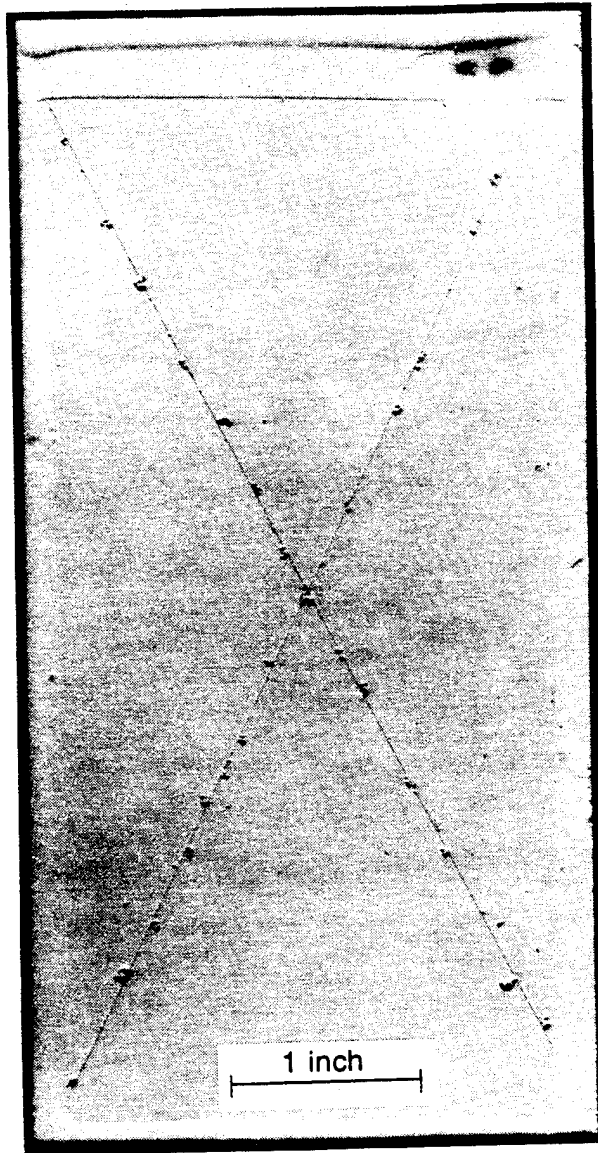


Figure B-4 Photograph of 1000-hour Filiform Corrosion of 7-Percent Q-Mo Epoxy-Polyamide Coating, Panel 96. Pass.

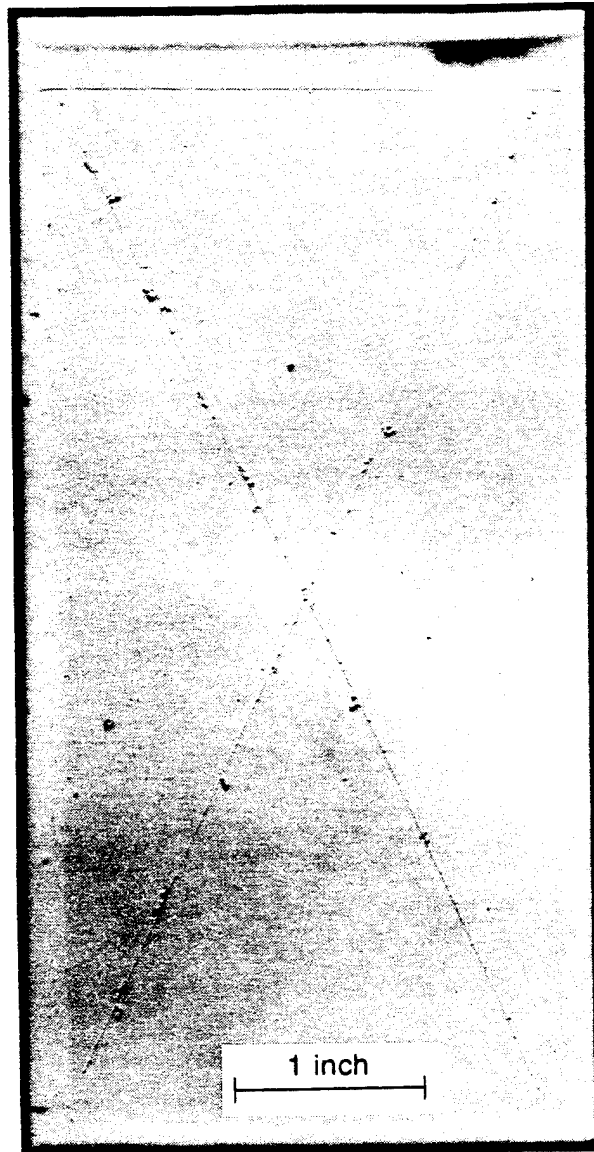


Figure B-5 Photograph of 1000-hour Filiform Corrosion of 9-Percent Q-Mo Epoxy-Polyamide Coating, Panel 103. Pass.

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